



Water-promoted catalytic hydrodechlorination of transformer oil-contained PCBs in liquid system under mild conditions



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ABSTRACT

The influences of solvent system on the hydrodechlorination (HDC) of transformer oil-contained PCBs with H₂ over Pd/C catalyst were studied. The addition of water in solvent system significantly accelerated the HDC reaction, which suggested its critical role for enabling Pd/C catalyst to keep high activity and stability. The mechanism of this phenomenon was studied through catalyst characterization (TEM, XRD and XPS), and the change of surface composition of Pd/C catalyst in different solvent in the HDC reaction was revealed. Above results indicated that water in isopropanol–water prevented NaCl accumulating on the surface of catalyst, which avoided the decline in activity and stability of the catalyst. On the basis of these studies, isopropanol–water (60/40, v/v) solvent system was developed to dispose high concentration transformer oil-contained PCBs, where the chloride atom removal ratio of transformer oil-contained PCBs at 2% (w/w) and 5% (w/w) concentration could reach 95.2% and 88.0% for 10 h under mild conditions respectively, and the Pd/C could be recovered and reused at least 10 times without any loss of catalytic activity.

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1. Introduction

Polychlorinated biphenyls (PCBs), which are a family of 209 chemical compounds with different numbers and positions of chlorine atoms on a biphenyl skeleton, have been widely used as an additive in electrical equipment. Commercial production of PCBs has been banned since the mid-1970s due to their toxicity of carcinogenicity, teratogenicity and mutagenicity, persistence in the environment, bioaccumulation and biomagnifications in the food chains [1,2]. Therefore, it is an urgent task to develop a proper decontamination of PCBs, which should be disposed by 2028 based on Stockholm Convention on Persistent Organic Pollutants (POPs) [3]. Currently, PCBs are mainly being destroyed by incineration [2], which consumes a large amount of fuel and probably produces highly toxic substances, including polychlorinated dibenzo-*p*-dioxin and polychlorinated dibenzo-furans (known as dioxins) [4,5]. In order to avoid the production of noxious chemicals, various destruction methods have been developed to detoxify PCBs including bioremediation [6,7], super/subcritical degradation [8,9], irradiation [10,11], photochemical degradation [12,13], oxidative degradation [14,15], reductive dechlorination [16–21], and so on. Unfortunately, most of these methods require harsh reaction conditions with special facilities, and many of them are

frequently incomplete. Among these methods mentioned above, reductive dechlorination that involves hydrogen cleavage of one or more C–Cl bonds, lowering the toxicity of chlorinated organic compounds (COCs) and preventing the formation of the hazardous by-products [20,21], was considered to be an environmental friendly method to detoxify.

For the reductive dechlorination, there are two different approaches: metal-mediated reductive dechlorination [16–19] and catalytic hydrodechlorination (HDC) [20,21]. Reductive dechlorination using modified zero-valent metal (zinc, iron, magnesium, ZVM), has been proposed for PCBs and other POPs dechlorination, but slow reaction rate and incomplete dechlorination have hindered the use of this approach in the field [22,23]. Recently, the ZVM system has been further advanced in previous research in the degradation of PCBs through deposition of a noble metal (such as Pd, Ni) on the substrate metal surface [22]. Yang et al. [17,24] propose that the enhanced reactivity of bimetal might be due to their reaction with highly reductive atomic hydrogen [H] adsorbed on a noble metal, which is generated by ZVM corrosion. However, the formation of metal (hydr)oxides on particle surface, which is produced by ZVM corrosion, is regarded as a key factor which affects the effectiveness of the bimetallic system [20,24,25]. Generally, the metal-mediated reductive dechlorination with either ZVM or bimetal is used to treat low concentrations and/or low chlorinated COCs with large amount of metal corrosion [20,26,27]. Compared with the metal-mediated reductive dechlorination, catalytic HDC is a more promising technology for its potential economic and

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environmental advantages and wide application for POPs dechlorination under relatively mild conditions [28]. Liquid-phase catalytic HDC reaction system satisfies not only sustainable chemistry but also economical requirements for advanced chemical processes development since the process occurs at ordinary temperature and the products can be recovered to use [29]. In the past decades, the research on discovery of catalysts has received broad attention in the liquid-phase HDC and a series of supported Pd, Rh, Ni, Pt catalyst have been developed [20,21,30–32]. Among these catalysts used in the liquid-phase HDC, supported Pd catalyst has been the most active one [21,29,33]. Additionally, active carbon is always used as catalyst support due to its large surface area and high stability [33].

Besides catalysts, solvent systems are considerably important factors to influence the liquid-phase HDC reaction [21,33–35]. However, little attention has been paid to solvent system in liquid-phase catalytic HDC. In the literatures reported, alcohols (mainly methanol and ethanol) are the most usual choice as solvent for liquid-phase HDC [33]. In our previous work, the Pd/C catalyst exhibited higher activity in alcohols than in alkanes, arenes and heterocycles in the HDC of COCs, and the HDC rate could be improved by adding water to the reaction solvents [36,37]. And some literature reported the similar results [34,35,38]. However, there is no agreement on the effect of added water. Gómez-Quero et al. [34,35] have linked the HDC activity dependency on dielectric constant (ϵ) to the capacity of the solvent to stabilize the arenium intermediate. Xia et al. [36,37] have suggested that higher HDC rate was achieved because of better removal of absorbed reaction products from the catalyst surface by added water.

In this study, our primary objective was to investigate the mechanism that the solvent system influences the activity and stability of catalysts in the HDC reaction of transformer oil-contained PCBs. The catalytic HDC of transformer oil-contained PCBs was performed in different solvents using 5% Pd/C(0) catalyst. In order to investigate the influence of solvent system on the catalyst, samples of the catalyst were analyzed by characterization (TEM, XRD and XPS). On the basis of these researches, a highly effective and environmental catalytic HDC solvent system was developed and applied to the disposal of transformer oil-contained PCBs at high concentration in liquid system under mild conditions.

2. Experimental

2.1. Chemicals

5% Pd/C(0) catalyst used in this study was prepared by impregnation from HCl solution of PdCl_2 . 5% Pd/C (Pd/C(1)) and 5% Pd/C (Cat.: 205680) (Pd/C(2)) were purchased from C&P Chemical Co., China and Sigma-Aldrich, USA, respectively. The three kinds of catalysts were not pre-treated before all experiments and only kept in a hermetical desicator. Transformer oil-contained PCBs were obtained in viscous liquid form from an incineration plant, China. The other reagents, such as solvents and bases, were analytical grade and were supplied by Sinopharm Chemical Reagent Co., Ltd. Deionized water was used in the reaction. The purities of hydrogen used in the experiments were more than 99.99%.

2.2. Transformer oil HDC studies

Each HDC run was carried out in a stirred three-necked flask with magnetic stirring at 300 rpm. The reaction vessel (50 ml) was placed in a temperature-controlled heating water bath with a precision of $\pm 1^\circ\text{C}$. Transformer oil-contained PCBs or 4-chlorobiphenyl was treated with hydrogen gas over 25 mg 5% Pd/C in different solutions (methanol, ethanol, isopropanol, and isopropanol–water) under mild conditions. NaOH (about 1.1 amounts of chlorine atoms of transformer oil-contained PCBs) was added to prevent catalyst

deactivation caused by HCl formed in the HDC reaction. The intermediate products and the composition of the reaction system in the HDC of transformer oil-contained PCBs were both determined by GC/MS.

2.3. Analytical methods

For the determination of transformer oil-contained PCBs, Gas chromatography/mass spectrometry (GC/MS) analysis was conducted using Thermo TRACE gas chromatograph coupled to ITQ 900 mass spectrometer operated in EI mode at 70 eV. The temperatures of the injection port, the MS transfer line and the ion source were all 280 °C. Samples were injected in the splitless mode onto a 30 m TR-5MS capillary column (0.25 mm I.D., 0.25 μm film thickness) using the following temperature program: the initial temperature of the column was 60 °C, held for 4.0 min, and the rate of the temperature increase was 25 °C/min up to 200 °C, and held for 2.0 min. Then, the increase rate was changed to 3 °C/min up to 280 °C, with a final hold time of 3 min. The carrier gas was He with a purity of 99.999%. The detection limit was 1 pg mL⁻¹.

Measurements of transformer oil-contained PCBs detected before and after the HDC reaction were divided into 11 groups on the basis of numbers of chlorine atoms on a biphenyl nucleus. The average chlorine atom number (ACN) is obtained as follows [39]:

$$\text{ACN} = \sum_{i=1}^j i C_{\text{PCB}_i}$$

C_{PCB_i} is the percentage of PCB with i chlorine atom(s); i is the number of chlorine atom(s) on a biphenyl nucleus.

There are overlaps between the retention times of PCBs with different numbers and positions of chlorine atoms, so the calculated ACNs which are used for evaluating PCB congeners mixtures and the HDC reaction, are only approximate but sufficient for following comparison.

2.4. Characterizations

The catalysts after the reaction in the liquid-phase system were separated from the solution, washed with the 95% ethanol, isopropanol and *n*-hexane to remove absorbed organic compounds, and dried in a N_2 flow at 200 °C prior to characterization analysis. The morphology of the fresh and used catalyst was characterized using transmission electron microscopy (TEM, a JEOL Model JEM-2011EM, Japan) at an accelerating voltage of 120 kV. The crushed catalysts are prepared first by dispersing in ethanol, and then two drops of the dispersed samples depositing on a copper mesh grid. X-ray diffractograms (XRD) of the catalysts were recorded with XRD-6100 of Shimadzu with a Cu K α radiation at 40 kV and 30 mA. The samples were scanned at a rate of 0.1°/s over the 5° $\leq 2\theta \leq$ 80° range with a scan time of 5 s step⁻¹. The surface composition of fresh and used catalysts was analyzed by X-ray photoelectron spectroscopy (Thermo Escalab 250Xi XPS) with Al K α radiation as the excitation source. Al K α radiation was operated at 15 kV and 14.9 mA. Binding-energy values were referred to the C (1s) peak at 285.0 eV.

3. Results and discussion

3.1. HDC pathway of transformer oil-contained PCBs in liquid-phase system

The catalytic HDC of transformer oil-contained PCBs was performed in a solution of NaOH over 5% Pd/C(0) catalyst under mild conditions [5]. Compared with four kinds of commercial

Table 1

Comparison of different kinds of PCB congener mixtures.

PCB (%) ^a	Transformer oil	Aroclor 1232	Aroclor 1242	Aroclor 1248	Aroclor 1262
TriCB	0	0.7	0	1.35	1.01
Biphenyl	0	5.34	0	0	0
MonoCBP	0	28.51	0.53	0	0.1
DiCBP	0.08	21.80	15.36	1.01	0.31
TriCBP	0.76	23.95	43.38	20.78	1.53
TetraCBP	0.50	17.72	36.27	58.81	0.73
PentaCBP	8.74	1.81	4.39	17.03	3.99
HexaCBP	43.76	0.16	0.07	1.02	29.25
HeptaCBP	38.19	0	0	0	40.45
OctaCBP	7.40	0	0	0	20.8
NonaCBP	0.58	0	0	0	1.83
ACN ^b	6.42	2.27	3.29	3.95	6.73

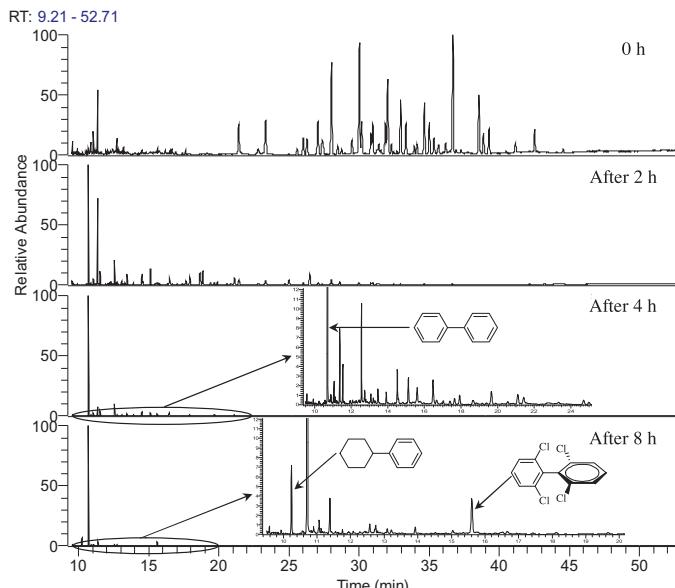
^a Yields were determined by GC/MS.^b The average chlorine atom number (ACN) is obtained as literature [39].

Fig. 1. HDC of transformer oil-contained PCBs in isopropanol over 5% Pd/C(0) catalyst with reaction time. Reaction conditions: isopropanol (50 ml), transformer oil-contained PCBs (250 mg), NaOH (180 mg, 4.5 mmol), 5% Pd/C(0) (25 mg), temperature (40 °C), H₂: 10 ml min⁻¹.

transformer oils, the transformer oil used in HDC reaction was mainly consist of high chlorinated congeners and closely matched the congener patterns of Aroclor 1262 by means of ACN (Table 1). As displayed in Fig. 1 by GC/MS analysis, the transformer oil-contained PCBs were transformed into lower chlorinated congeners as the proceeding of the reaction. Progress of product and intermediate distributions versus reaction time were given in Fig. 2. The concentrations of the higher chlorinated PCBs congeners (with 6–9 chlorines) decreased sharply with the reaction time, and the concentrations of less chlorinated PCBs congeners (with 1–5 chlorines) increased to concentration maximums and then decreased sluggishly. The concentration of biphenyl and cyclohexylbenzene increased gradually with the reaction time. Similar patterns were observed for the other runs. Meanwhile, cyclohexylbenzene was the only hydrogenation product of aromatic ring detected by

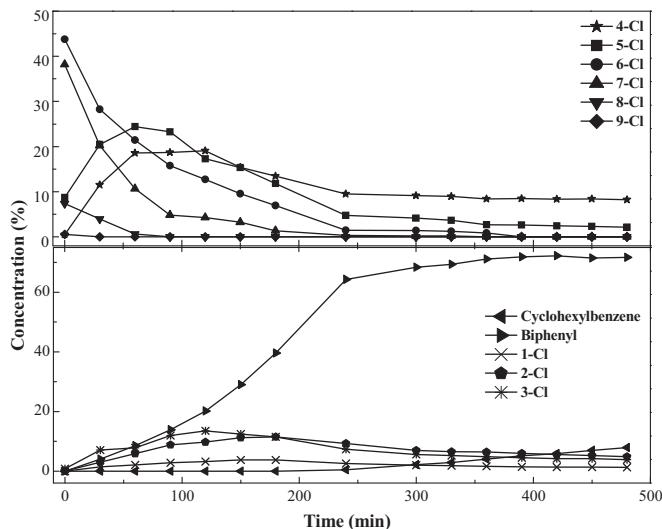
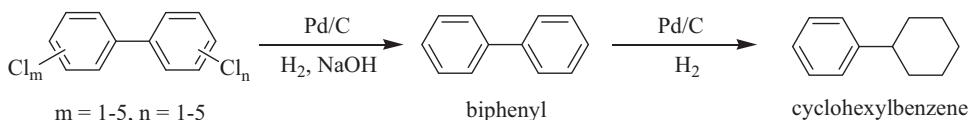


Fig. 2. Reaction profiles of catalytic HDC of transformer oil-contained PCBs in isopropanol over 5% Pd/C(0) catalyst. Reaction conditions: isopropanol (50 ml), transformer oil-contained PCBs (250 mg), NaOH (180 mg, 4.5 mmol), 5% Pd/C(0) (25 mg), temperature (40 °C), H₂: 10 ml min⁻¹.

the chromatogram of GC-MS in the catalytic HDC of transformer oil-contained PCBs. This might be due to the mild reaction conditions in our research. Therefore, the reaction pathway involves multisteps that PCBs was completely dechlorinated to produce biphenyl, and then biphenyl was further hydrogenated to form cyclohexylbenzene (Scheme 1).

After the HDC reaction, about 10% of 2,2',6,6'-tetrachlorobiphenyl (2,2',6,6'-TCBP) were observed in the samples by GC/MS analysis (Figs. 1 and 2). As the mainly incomplete hydrodechlorinated intermediate product in the HDC of transformer oil-contained PCBs, 2,2',6,6'-TCBP was a fully *ortho*-substituted PCB congener, and two benzene rings of such biphenyl should twist around each other to form steric hindrance of *ortho*-chlorines. Because of the effect of steric hindrance, the HDC of 2,2',6,6'-TCBP was markedly delayed. Fortunately, 2,2',6,6'-TCBP did not cause as much serious dioxin-like toxicity and carcinogenicity as co-planar PCBs congeners due to its non-planar molecular structure unlike



Scheme 1. The postulated HDC pathway of transformer oil-contained PCBs in liquid-phase system.

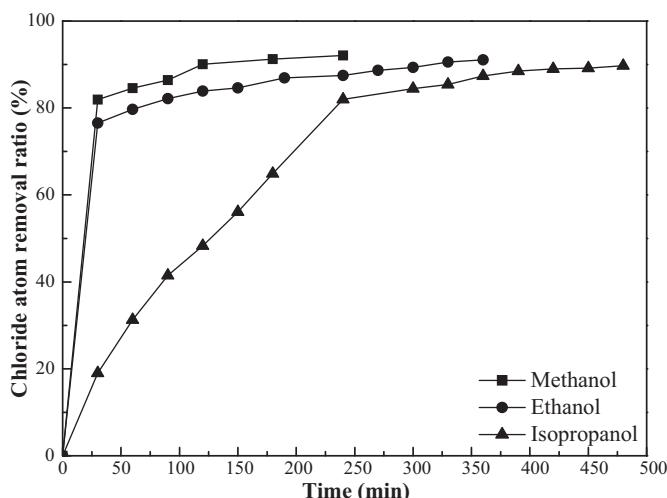


Fig. 3. HDC of transformer oil-contained PCBs in different alcohols over 5% Pd/C(0) catalyst. Reaction conditions: each solvent (50 ml), transformer oil-contained PCBs (250 mg), NaOH (180 mg, 4.5 mmol), 5% Pd/C(0) (25 mg), temperature (40 °C), H₂: 10 ml min⁻¹.

dioxin [2]. Therefore, the liquid-phase catalytic HDC could efficiently detoxify PCBs even though there was some 2,2',6,6'-TCBP left after the reaction.

3.2. The solvent effect on the HDC

Reaction media plays an important role on reaction activity of the liquid-phase catalytic HDC [34,35,38]. For the HDC of COCs, Pd/C catalyst exhibited higher activity in alcohols than in alkanes, arenes and heterocycles [36]. The phenomenon was in agreement with the results obtained by Gómez-Quero [34,35]. Therefore, alcohols were selected as the solvent in the HDC reaction.

Here, the catalytic HDC of transformer oil-contained PCBs was performed in different alcohols using 5% Pd/C(0) catalyst under mild conditions. As shown in Fig. 3, the chloride atom removal ratio of transformer oil-contained PCBs was found to be in the order of methanol > ethanol > isopropanol, which was consistent with the order of solvent polarity. It suggested that the HDC rate increased with the solvent polarity increasing. This is consistent with findings of Gómez-Quero et al. [35], who observed higher initial HDC rates for 2,4-dichlorophenol with increasing dielectric constants of solvent. They suggest that solvent with high dielectric constant (ϵ) has strong ionic force to stabilize the electropositive arenium intermediate, and then enhance the reaction efficiency [35]. Moreover, it was found that the initial period of reaction (30 min for methanol and ethanol, 240 min for isopropanol), the chloride atom removal ratio was very high, which meant 5% Pd/C(0) catalyst owned high activity. However, as the proceeding of the HDC reaction, the chloride atom removal ratio increased very slowly and could not reach 100% even after a long reaction time of several hours, indicating the activity of 5% Pd/C(0) catalyst decreased sharply in this period. It would be reasonable to presume that for catalytic HDC of transformer oil-contained PCBs, alcohols were not the most suitable solvent because 5% Pd/C(0) catalyst could not keep high activity during the whole course and the removal ratio of chloride atom could not reach 100% within a certain time.

It was reported that water was the best solvent among all the solvents used for the HDC of 4-chlorophenol [37]. Yet, transformer oil-contained PCBs are insoluble in water. Therefore, a mixed solvent of water and alcohol was designed as the solvent for further study. Li et al. reported that the solubility of PCBs in alcohols decreases with an increase of the polarity of alcohols [40]. And we also found that transformer oil-contained PCBs

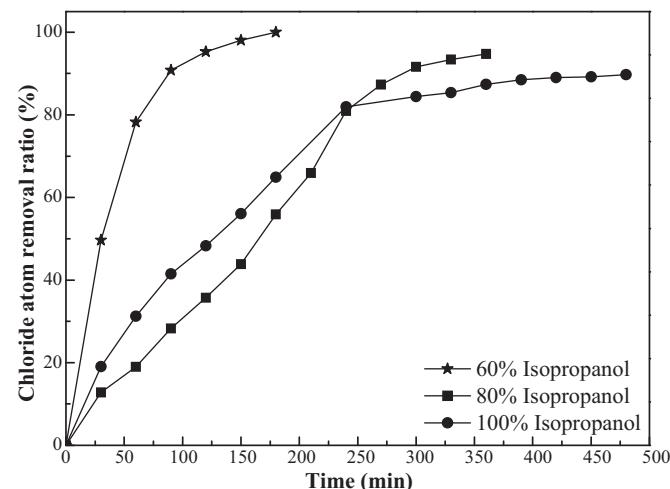


Fig. 4. HDC of transformer oil-contained PCBs in various isopropanol–water mixtures. Reaction conditions: each solvent (50 ml), transformer oil-contained PCBs (250 mg), NaOH (180 mg, 4.5 mmol), 5% Pd/C(0) (25 mg), temperature (40 °C), H₂: 10 ml min⁻¹.

cannot be dissolved well in methanol–water and ethanol–water because of its poor solubility in these solvent system at 40 °C. Therefore, it is not suitable to carry out the HDC of transformer oil-contained PCBs in methanol–water and ethanol–water. Considering the solubility and reactivity of transformer oil in different solvents, isopropanol–water was a good choice [40]. Fig. 4 shows the HDC of transformer oil-contained PCBs in three isopropanol–water mixtures. The solubility of transformer oil-contained PCBs in isopropanol–water decreases with an increase of the concentration of water in the mixture, and PCBs cannot be dissolved completely when the concentration of water is more than 40%. Therefore, the HDC reaction in isopropanol–water (concentration of isopropanol less than 60%) was not performed for the poor solubility of transformer oil in this solvent at 40 °C. It could be seen from Fig. 4 that the chloride atom removal ratio of transformer oil-contained PCBs obviously increases with an increase of the content of water in isopropanol–water. Moreover, the chloride atom removal ratio could reach 100% and 2,2',6,6'-TCBP could be completely hydrodechlorinated within 180 min in isopropanol–water (60/40, v/v), which showed that 5% Pd/C(0) catalyst owned high activity in this solvent system.

Subsequently, the stability of 5% Pd/C(0) catalyst used in isopropanol and isopropanol–water (60/40, v/v) were investigated. Because of the complexity of the GC/MS analysis for transformer oil-contained PCBs, 4-chlorobiphenyl was selected as the representative compound. The HDC of 4-chlorobiphenyl (1%, w/w) was repeated 10 times with the catalyst recovered after each reaction. Fig. 5 showed the conversion change in the repeated reaction with 5% Pd/C(0) catalyst reuse in isopropanol and isopropanol–water (60/40, v/v) respectively. In isopropanol, the conversion was 100% at 60 min for the first time and then dropped significantly to 50.1% in the 4th run. Yet in isopropanol–water, the conversion reached 100% (60/40, v/v) at 15 min. These results demonstrated that 5% Pd/C(0) catalyst possessed high activity and stability when isopropanol–water (60/40, v/v) was used as solvent, and could be reused at least 10 times with almost the same activity for the HDC of 4-chlorobiphenyl under mild conditions.

3.3. The role of water for the catalysts

In the above study, it was found that water played an important role in the HDC reactivity of transformer oil-contained PCBs. The reason for this phenomenon is still a matter of some debate as

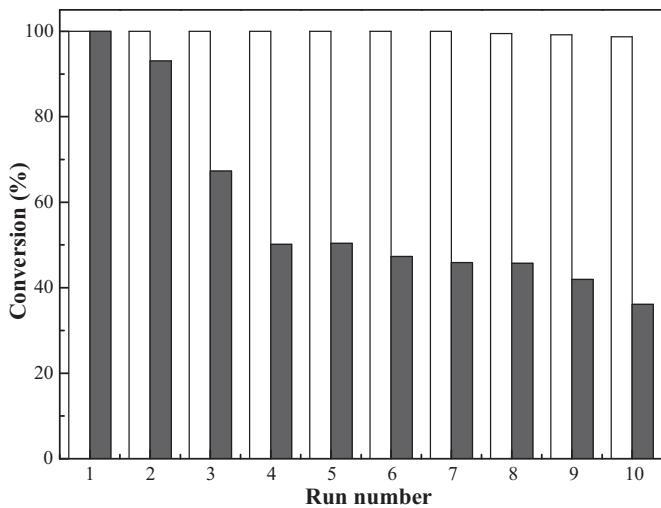


Fig. 5. Repeated HDC of 4-chlorobiphenyl in isopropanol–water (60/40, v/v) for 15 min (open square) and isopropanol for 60 min (filled square). Reaction conditions: each solvent (50 ml), 4-chlorobiphenyl (0.5 g, 2.65 mmol), NaOH (120 mg, 2.9 mmol), 5% Pd/C(0) (25 mg), temperature (40 °C), H₂: 10 ml min⁻¹.

there are many instances in which the solvent has participated in the HDC reaction [21]. Gómez-Quero et al. [34] have linked the HDC activity dependency on dielectric constant (ϵ) to the capacity of the solvent to stabilize the arenium intermediate. It was presumed that solvent system had a significant influence on the surface reaction of the catalyst in our previous literatures [36,37]. However, there is no evidence for this hypothesis. In order to get accurate evidence for the role of water, samples of catalysts were analyzed by characterizations (TEM, XRD and XPS).

Firstly, the 5% Pd/C catalysts before and after 10 times HDC reactions in isopropanol and isopropanol–water (60/40, v/v) were analyzed by TEM. The representative TEM images of the 5% Pd/C(0) catalysts were given in Fig. 6 (the mean particle size and particle distribution of TEM images are provided in the Fig. S1 and Table S1 in Supplementary data). As illustrated in Fig. 6A and 6B, the morphology of 5% Pd/C(0) catalyst reused for 10 times in isopropanol–water (60/40, v/v) was almost the same as that of the fresh catalyst. On the contrary, the morphology of 5% Pd/C(0) catalyst reused for 10 times in isopropanol changed a lot, and amounts of crystals deposited on the surface of the catalyst (Fig. 6C and D). In order to get more information about the composition of crystal, XRD analyses of the 5% Pd/C(0) catalysts were performed. For the XRD

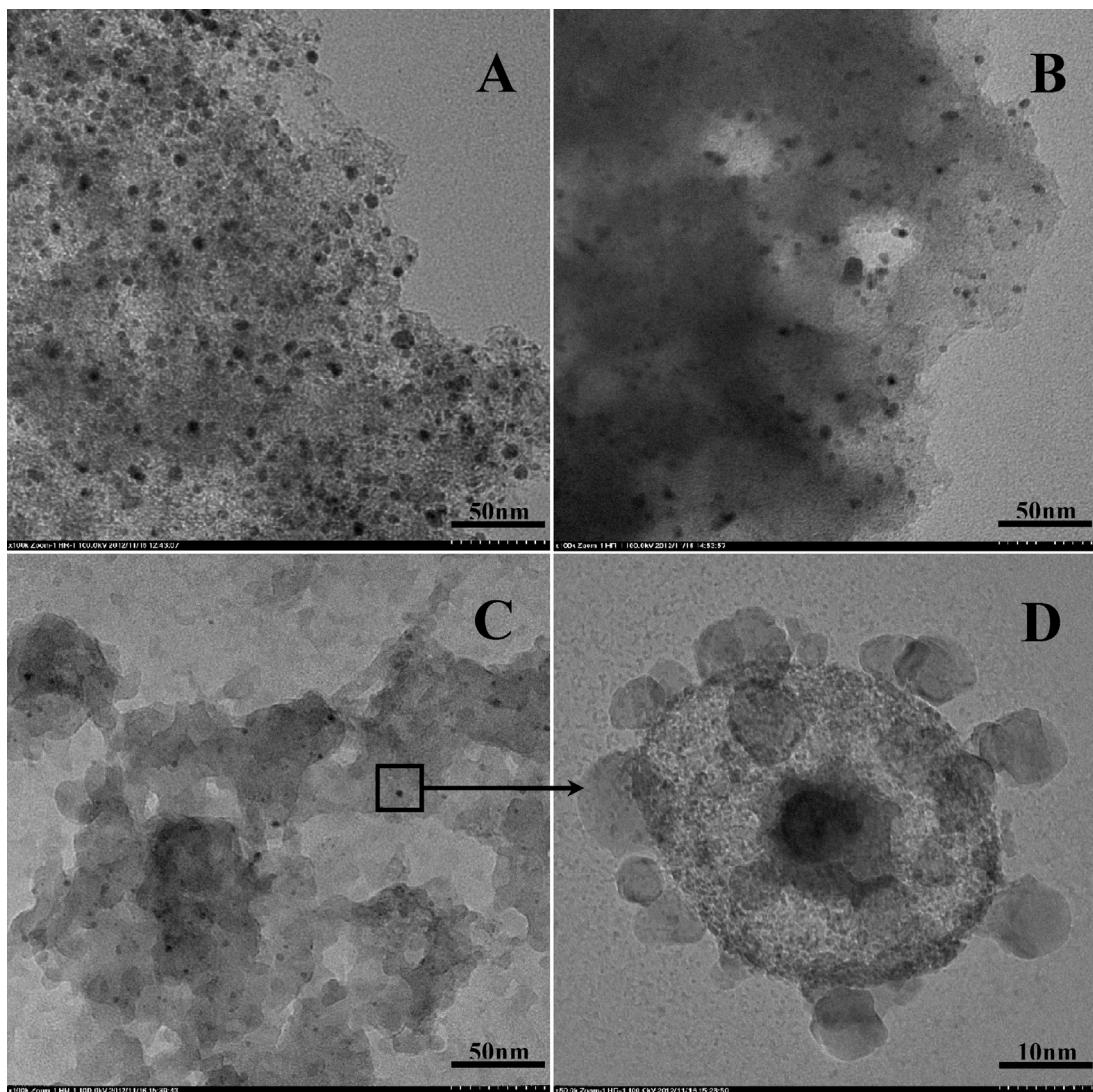


Fig. 6. TEM images of the 5% Pd/C(0) catalysts fresh (A), after the 10 time dechlorination reaction in isopropanol–water (60/40, v/v) (B), after the 10 time dechlorination reaction in isopropanol (C), and D is amplified image the area marked on C.

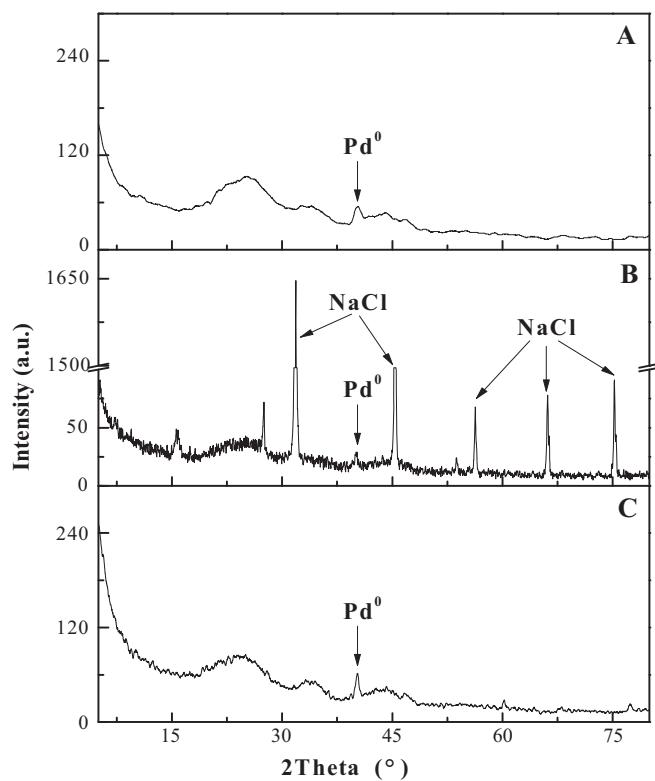


Fig. 7. XRD patterns of (A) The fresh 5% Pd/C(0) catalyst, (B) the 5% Pd/C(0) catalyst used in isopropanol, (C) the 5% Pd/C(0) catalyst used in isopropanol–water (60/40, v/v).

patterns of three kinds of 5% Pd/C(0) catalysts (Fig. 7), the peak at $2\theta = 40.1^\circ$ could be indexed to (1 1 1) Pd plane. Except for the peak of (1 1 1) Pd, no peaks were found in the XRD pattern of 5% Pd/C(0) catalyst used in isopropanol–water (60/40, v/v) (Fig. 7C),

which further meant that there was no crystal deposited on the surface of the 5% Pd/C(0) catalyst. However, there were five more peaks at $2\theta = 31.9^\circ, 45.4^\circ, 56.3^\circ, 66.2^\circ$ and 75.2° on the XRD pattern of 5% Pd/C(0) catalyst used in isopropanol (Fig. 7B and Table S2 in Supplementary data). Compared with JCPDS (Joint Committee on Powder Diffraction Standards) standard card, the five peaks were respectively identified to (2 0 0), (2 2 0), (2 2 2), (4 0 0) and (4 2 0) NaCl planes. It would be reasonable to demonstrate that the crystals accumulated on the surface of the catalyst used in isopropanol were NaCl.

Furthermore, XPS analyses were carried out to get more information about the surface composition of the Pd/C(0) catalyst before and after one time HDC reaction in three kinds of isopropanol–water solvents (isopropanol, 80% isopropanol and 60% isopropanol). As depicted in Fig. 8 (binding energies and atomic ratios of Cl/C and Na/C from XPS are provided in the Table S3 in Supplementary data), an intense C (1s) peak due to the active carbon support of Pd/C catalyst was observed at 284.5 eV. The XPS spectrum of Pd (3d_{3/2}, 3d_{5/2}) peaks, which were detected at 340.8 and 335.5 eV respectively, were in good agreement with the values for zero-valence Pd metal [41]. Meanwhile, the binding energy of 3d_{3/2} at 342.2 eV and 3d_{5/2} at 337.2 eV is consistent with the presence of Pd (II) state [5,8]. Compared with the XPS spectrum of fresh catalyst, there were intense Cl (2p) peak and Na (1s) peak appeared at 200.0 eV and 1072.2 eV respectively, with a decrease in the intensity of the C and Pd peaks (Fig. 8B) of the catalyst used in isopropanol. The binding energy of Cl (2p) and Na (1s) agreed with that of NaCl accumulated on Pd/C(0) catalyst. In the XPS spectrum of the catalyst used in the HDC reaction, the peaks of Cl (2p) and Na (1s) decreased as water concentration increased, and completely disappeared when the water concentration in the reaction solvent reached to 40% (Fig. 8B–D). These results further confirmed that the crystals accumulated on the surface of the catalyst used in isopropanol were NaCl, and water in isopropanol–water could prevent NaCl from depositing on surface of the catalyst.

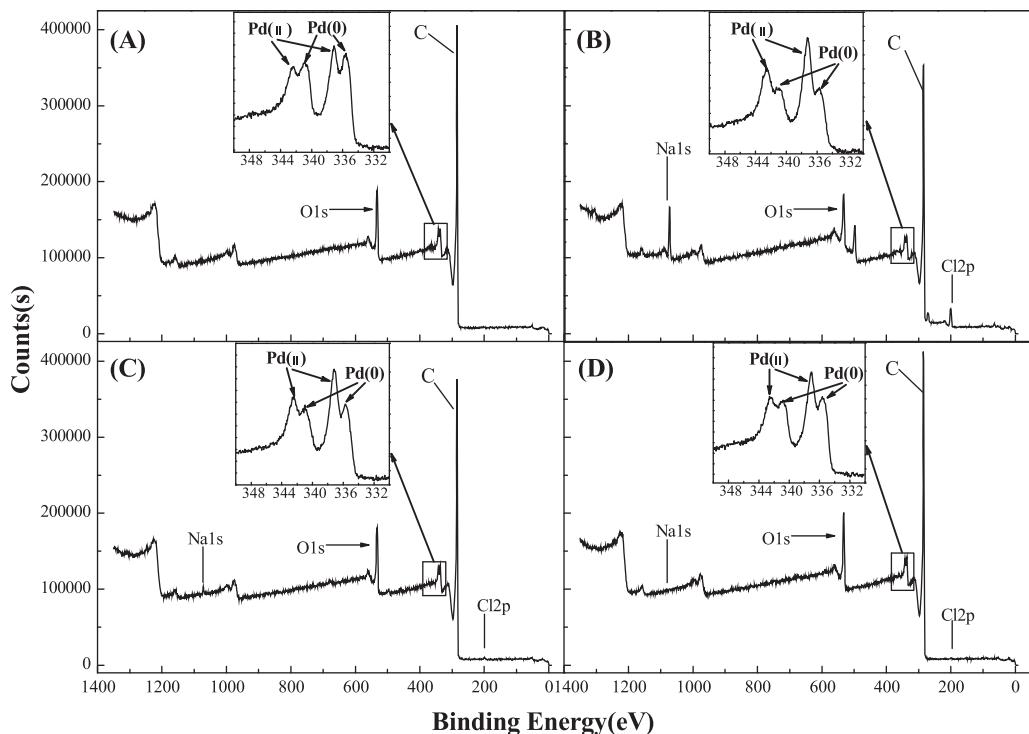
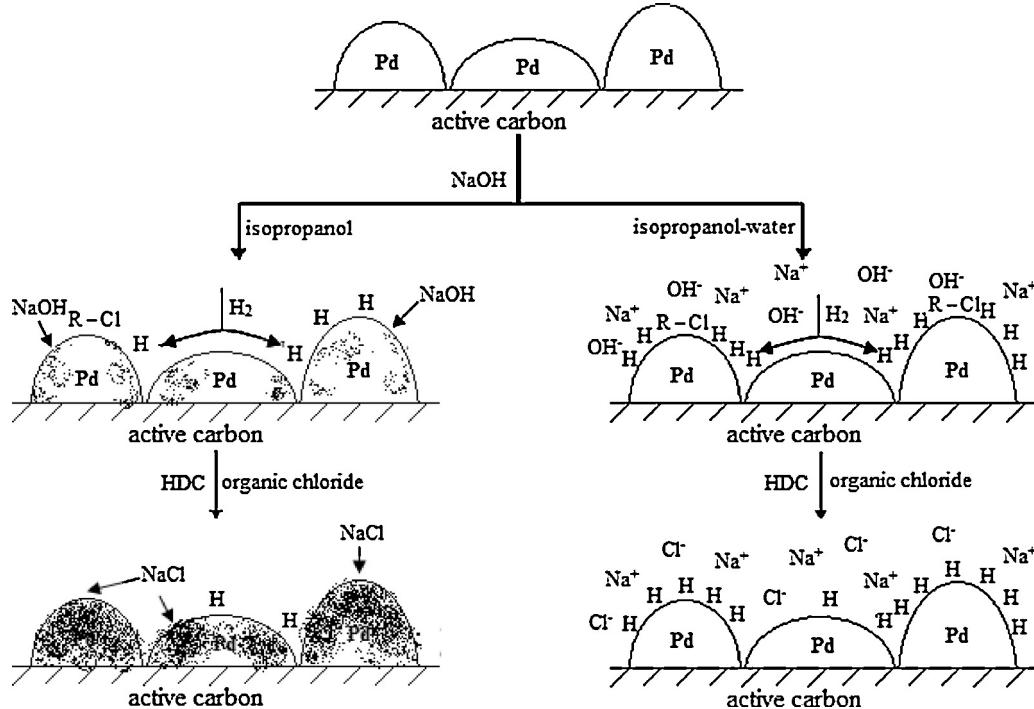


Fig. 8. XPS spectrum of the 5% Pd/C(0) catalysts before and after the HDC reaction of different solvents. (A) The fresh 5% Pd/C(0) catalyst, (B) the 5% Pd/C(0) catalyst used in isopropanol, (C) the 5% Pd/C(0) catalyst used in isopropanol–water (80/20, v/v), (D) the 5% Pd/C(0) catalyst used in isopropanol–water (60/40, v/v).



Scheme 2. The change of surface composition of 5% Pd/C(0) in isopropanol and isopropanol–water in the HDC of transformer oil-contained PCBs.

It is widely accepted that HCl, byproduct of the HDC reaction, was the main reason for catalyst deactivation as it could attack the catalyst to form metal chlorides [5,37,42]. In this study, NaOH, act as a proton acceptor, was added to prevent catalyst deactivation caused by HCl, and NaCl was the product of the neutralization of HCl and NaOH. In isopropanol, NaCl accumulated on the active sites and surface of the catalyst, which was demonstrated by the results obtained from the characterization analyses (TEM, XRD and XPS). The accumulation of NaCl and NaOH could block catalytic active sites and hindered the absorption and activation of hydrogen gas and PCBs [36,42], and thus could cause the decline in activity and stability of the catalyst. Similar result has been reported for the HDC of dioxins over Pd/ γ -Al₂O₃ catalyst [5]. Therefore, the activity of the catalyst decreased as the proceeding of the HDC reaction in alcohols (Fig. 3). The change of surface composition of 5% Pd/C(0) in isopropanol and isopropanol–water in the HDC of transformer oil-contained PCBs is shown in Scheme 2. In isopropanol–water (60/40, v/v), the presence of water enable NaCl to ionize as Na⁺ and Cl[−] easily and prevented NaCl from depositing on active sites and surface of the catalyst, thereby avoiding the decline in the activity and stability of the catalyst. On the other hand, the isopropanol had a weaker solvating power for NaOH than isopropanol–water [43]. The added NaOH was easily dissolved in isopropanol–water as Na⁺ and OH[−] which were bound by water molecules through H-binding. The water in isopropanol–water advanced solvating power of solvent system for NaOH effectively and lowered the sensitivity of Pd/C catalyst for poisoning, resulting in a high activity and stability of the catalyst (Figs. 4 and 5). In summary, the presence of water in isopropanol–water advanced the inorganic salts (NaOH and NaCl) to be dissolved and ionized, which prevented the inorganic salts from accumulating on the surface of catalyst and thereby enabled the catalyst to keep high activity and stability.

3.4. The applicability of isopropanol–water solvent system

We demonstrated the mechanism of phenomenon that water in isopropanol–water effectively prevented the inorganic salt

accumulating on surface of the catalyst and thus enabled the catalyst to keep high activity and stability. Then the isopropanol–water (60/40, v/v) solvent system was developed for catalytic HDC over Pd/C catalyst. In order to test the applicability of this solvent system, two kinds of commercial Pd/C catalysts were chose to apply in the catalytic HDC. From the data of Fig. 9, 5% Pd/C(1) and 5% Pd/C(2) had almost the same catalytic activity as the 5% Pd/C(0), which demonstrated that the isopropanol–water (60/40, v/v) solvent system could be used to dispose the transformer oil-contained PCBs with the commercial Pd/C catalyst. Furthermore, the catalytic HDC of high concentrations transformer oil-contained PCBs were performed in isopropanol–water (60/40, v/v) solvent system with 5% Pd/C(0). As shown in Fig. 10, the chloride atom

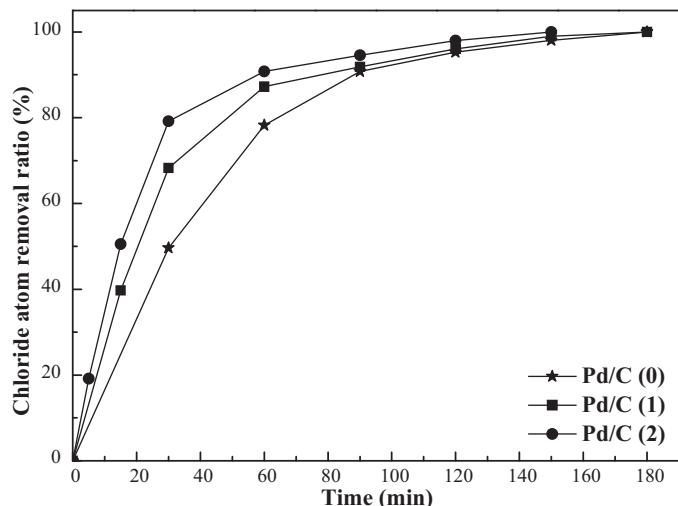


Fig. 9. HDC of transformer oil-contained PCBs in isopropanol–water (60/40, v/v) by using 5% Pd/C(0), 5% Pd/C(1) and 5% Pd/C(2). Reaction conditions: each solvent (50 ml), transformer oil-contained PCBs (250 mg), NaOH (180 mg, 4.5 mmol), 5% Pd/C (25 mg), temperature (40 °C), H₂: 10 ml min^{−1}.

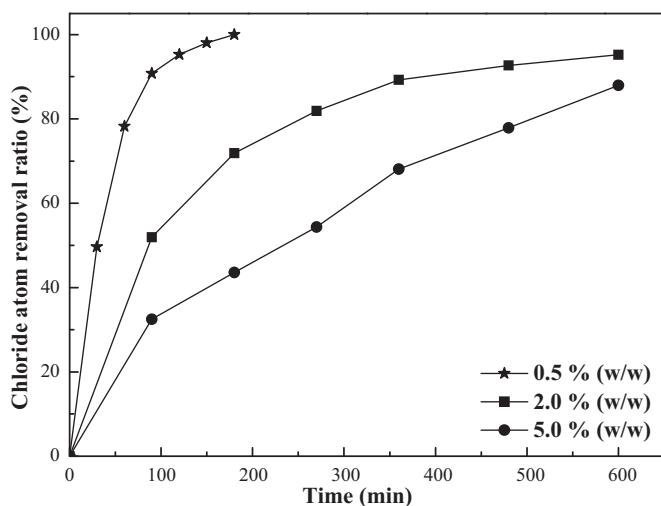


Fig. 10. HDC of different concentration of transformer oil-contained PCBs in isopropanol–water (60/40, v/v) over 5% Pd/C(0). Reaction conditions: each solvent (50 mL), 5% Pd/C(0) (25 mg), (★) transformer oil-contained PCBs (250 mg), NaOH (180 mg, 4.5 mmol), temperature (40 °C), pressure (0.1 MPa); (■) transformer oil-contained PCBs (1.0 g), NaOH (720 mg, 18.0 mmol), temperature (80 °C), pressure (0.4 MPa); and (●) transformer oil-contained PCBs (2.5 g), NaOH (1.8 g, 45.0 mmol), temperature (80 °C), pressure (0.4 MPa).

removal ratio of transformer oil-contained PCBs at 2% (w/w) and 5% (w/w) concentration could reach 95.2% and 88.0% for 10 h. Moreover, the activity of the 5% Pd/C(0) catalyst was still at high level after 10 h reaction. Above results suggested that the developed isopropanol–water (60/40, v/v) was a practical and efficient solvent system for disposing the high concentration transformer oil-contained PCBs with commercial Pd/C catalyst.

4. Conclusions

We demonstrated that water in isopropanol–water efficiently prevented the decline in the activity and stability of Pd/C catalyst in HDC of transformer oil-contained PCBs, and clarified the mechanism of this phenomenon by characterizations. On the basis of the mechanism above, the isopropanol–water (60/40, v/v) solvent system was developed for catalytic HDC with H₂ over Pd/C catalyst and applied to catalytic HDC of transformer oil-contained PCBs with two commercial catalysts. Furthermore, the solvent system was applicable to the complete HDC of high concentration transformer oil-contained PCBs under mild conditions and the catalyst, 5% Pd/C, could be recovered and reused. This report provided a practical strategy to establish solvent system which was suitable for application in catalytic HDC of high concentration transformer oil-contained PCBs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.07.067>.

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